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Components Influence on Dielectric Properties of Ferroelectric Composite Materials

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Abstract

The dielectric properties of ferroelectric composite $(NH_4HSO_4)_x/(PbTiO_3)_{1-x}$ is studied for x ranging from 0,00 to 0,50. Measurements of permittivity were performed by heating-cooling mode temperature range from 130 K to 380 K. The value of the temperature interval of existence of the ferroelectric phase increases by ~5 degrees and independent at the volume fraction of particulate inclusions in composites. It is shown that the inclusion of $PbTiO_3$ particles gives rise to hysteresis upper temperature phase transition, which may indicate a change in the type of phase transition of the second order on the first-order phase transition.

Keywords: ferroelectrics, phase transition, composite

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1. Introduction

Ferroelectric composites have non-linear dielectric properties, depending on external conditions. Currently, such composite materials are widely used in microelectronics, instrumentation, and materials for space due to their extraordinary physical properties. For example, thermistors with abnormally high positive coefficient of resistance are used in instrumentation engineering as active elements of measuring, signaling, and safety devices [1]. In addition, some ferroelectric materials exhibit high radiation resistance, which allows their use as coatings for spacecraft. Such coatings with inclusion of ferroelectric particles are capable of creating an outer protection of the spacecraft from the excess electric charge during the flight [2].

Dielectric properties of ferroelectric composites were investigated in Refs. [3, 4]. It is shown that an increase in the volume fraction of particular inclusions in composites $(KNO_3)_{1-x}/(BaTiO_3)_x$ and $(KNO_3)_{1-x}/(PbTiO_3)_x$ stabilizes their ferroelectric phase. Therefore, further studies of ferroelectric composites of different compositions and varying percentage of inclusions of particles presents a scientific interest.

In this paper, we investigate the dielectric properties of ferroelectric composite $(NH_4HSO_4)_x/(PbTiO_3)_{1-x}$. Earlier, it was found that there was an expansion of the temperature interval of the ferroelectric phase existence for ammonium hydrogen sulfate particles in the nanoscale matrices caused by reducing the temperature of the lower

phase transition and also increasing the width of the hysteresis lower temperature phase transition [5 and references therein].

2. Methods

Ammonium hydrogen sulfate NH_4HSO_4 ferroelectric is in the temperature range from 160 K to 270 K at heating and from 154 K to 270 K at cooling. The value of spontaneous polarization at 260 K is 0,4 °C/cm^2 and reaches its maximum of 0,8 °C/cm^2 at 154 K. Structure NH_4HSO_4 belongs to the space group *Pc* in ferroelectric phase, to the space group $P2_1/c$ at room temperature and to the space group *Pc* at low temperatures. Both phase transitions are associated with the processes of SO_4 tetrahedra ordering [6].

Lead titanate $PbTiO_3$ is a ferroelectric perovskite. At room temperature, it has a tetragonal structure. The magnitude of the spontaneous polarization is ~57 °C/cm^2 [7]. When heated to the Curie temperature of 768 K, the ferroelectric undergoes phase transition from the tetragonal to the cubic nonpolar polar phase [8].

For research, composite samples $(NH_4HSO_4)_x/(PbTiO_3)_{1-x}$ were prepared with x = 0,10; 0,20; 0,30; 0,40; 0,50. Respective volume proportions of ammonium hydrogen and lead titanate powders were mixed and pressed at 6000 kg/cm^2 into tablets of 13 mm diameter and ~1 mm thickness. Measurements of dielectric constant were performed in the heating mode, during cooling in the temperature range from 130 K to 380 K at a rate of 1 deg/min in the frequency range from 0,1 Hz to 10 MHz using a broadband dielectric spectrometer Novocontrol. We used silver paste for the electrodes. To remove adsorbed water, composite samples were pre-warmed to 380 K.

3. Results

Figure 1 shows the temperature dependence of the permittivity of the composite samples $(NH_4HSO_4)_x/(PbTiO_3)_{1-x}$ of different compositions. As reference, was used a sample of polycrystalline ammonium hydrogen sulfate (x = 0,00). The maxima of the dependence for polycrystalline NH_4HSO_4 corresponding to phase transitions are located at the points T_1 = 166 K and T_2 = 272 K, which is 6 K and 2 K higher than the phase transition temperature of the single crystal of ammonium hydrogen sulfate. This may be due to the mechanical stress of the sample, crystal deformation, charge on the crystal surface, or air gap between the crystals preventing the propagation of domains and domain wall motion. On the graphs $\varepsilon'(T)$ (Fig. 1) for composite samples with a volume fraction of lead titanate particles $0{,}10 \le x \le 0{,}40$ there are two peaks of the permittivity. The upper peak corresponding to the transition from paraelectric to ferroelectric phase is near the bottom temperature 270 K. The peak corresponding to the transition between paraelectric and ferroelectric phases is 3-6 degrees less than the temperature of the polycrystalline NH_4HSO_4. For the composite sample $(NH_4HSO_4)_x/(PbTiO_3)_{1-x}$ with a volume fraction of inclusions x = 0,50 peaks corresponding to phase transitions are not observed as well as for the composite $(KNO_3)_{0,50}(BaTiO_3)_{0,50}$ [3, 4].

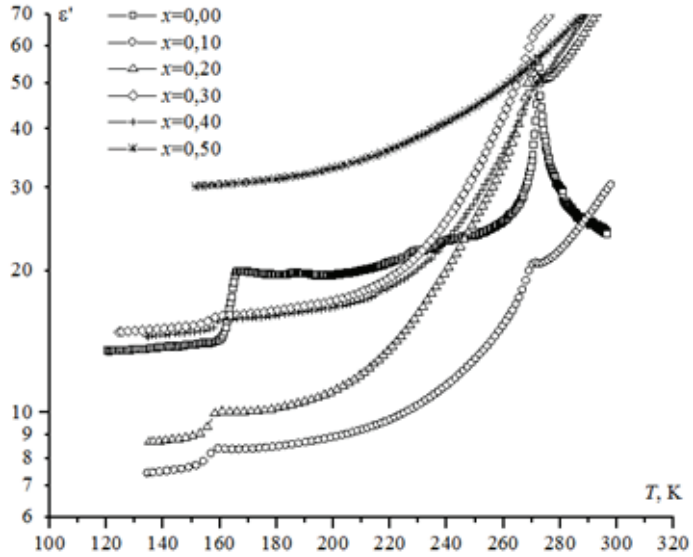

Figure 1: Temperature dependence of ε' at heating for composite samples $(NH_4HSO_4)_x/(PbTiO_3)_{1-x}$ at frequency 1 MHz.

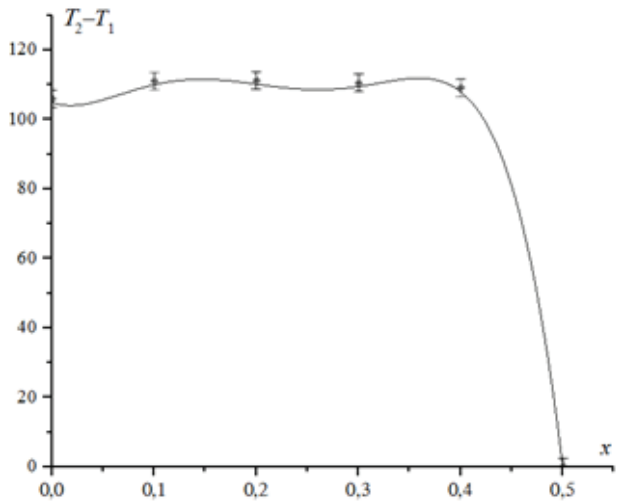

Figure 2: The composition dependence of the temperature interval of existence of ferroelectric phase.

Figure 2 shows that width temperature interval of the ferroelectric phase ammonium hydrogen sulfate in composite with a volume fraction of particle inclusions from 0,10 to 0,50 by heating is expanded by ~5 degrees as compared with pure polycrystalline NH_4HSO_4 and it is independent on the volume fraction of inclusions. In order to explain the stabilization of the ferroelectric phase ammonium hydrogen sulfate in composite, we use the expansion of the free energy in accordance with the Landau theory [9], where the value of the polarization plays the role of the order parameter. In addition, it is necessary to consider an additional contribution due to an electric dipole interaction of particles $PbTiO_3$ with the surrounding particle matrix NH_4HSO_4.

The volume fraction of particles in a sample composite inclusions *x*	T_1 (K) cooling/warming	Hysteresis width (K)	T_2 (K) cooling/warming	Hysteresis width (K)
x=0,10	159,1/154	5,1	270/272,6	-2,6
x=0,20	158,5/153,4	5,1	270/273	-3
x=0,30	160,7/155	5,7	271,3/270,5	0,8
x=0,40	160,9/155,7	5,2	270/271	1

Table 1: The temperatures of the upper and lower phase transition during heating and cooling, the width of the hysteresis loop for the investigated samples.

Thus, the free energy of the ferroelectric particle systems (in the absence of an external electric field) can be written as:

$$F = \sum_i \int_V \left(\frac{1}{2}\alpha P_i^2 + \frac{1}{4}\beta P_i^4 + \frac{1}{2}\delta \left(\nabla P_i\right)^2 \right) dV_i + F_{dd}, \quad (1)$$

where $F_{dd} = \sum_{i,j} \int_V \int_V \left[\frac{p_i^* p_j^*}{r_{ij}^3} - \frac{3\left(r_{ij} p_i^*\right)\left(r_{ij} p_j^*\right)}{r_{ij}^5} \right] dV_i dV_j$, V_i, V_j and p_i, p_j – volumes and polarization particles NH_4HSO_4 and $PbTiO_3$, respectively, r_{ij} – extrapolation a length, which is determined by the distribution of particles in the sample. The energy of the dipole-dipole interaction ΔF_{dd} depending on the location and orientation of the dipole moments of the particles can have both positive and negative values. However, due to general physical considerations we can conclude that the dipole moments are oriented in NH_4HSO_4 particles so as to compensate field $PbTiO_3$ particles when ΔF_{dd}>0, thus increasing the ferroelectric stability. This can be explained by the fact that each dipole reorientation is difficult, as it requires additional overcoming of the potential barrier formed by the dipole moments of $PbTiO_3$ particles.

The absence of peaks corresponding to phase transitions, for samples *x*=0,50 can be explained as follows. With increase in the proportion of lead titanate particles in the composite, the distance between the titanate is reduced. This leads to the fact that the field of lead titanate particles closes on itself, and ferroelectric properties of the ammonium hydrogen sulfate in the composite will not appear.

Figure 3 shows the temperature dependence of the permittivity for the composite samples $(NH_4HSO_4)_x/(PbTiO_3)_{1-x}$ in cycle heating-cooling for the upper phase transition. Studies have shown that the inclusion of $PbTiO_3$ particles give rise to the upper temperature hysteresis of the phase transition. In pure NH_4HSO_4 there is no hysteresis, as this transition is of the second order. The observed temperature hysteresis may indicate a change in the type of phase transition from the second order to the first order one.

Table 1 presents the lower and upper phase transition temperatures during heating and cooling, for the hysteresis width of the samples.

To understand the thermal hysteresis, it should be noted that the Hamiltonian of dipole-dipole interactions above and below the phase transition has a different size, since two systems with ready dipole moments interact in the ferroelectric phase.

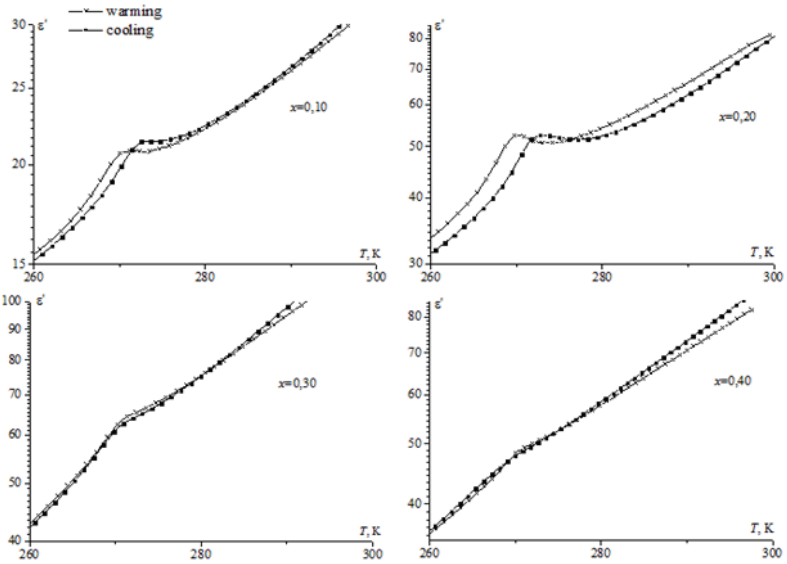

Figure 3: The temperature dependence of the permittivity of the composite samples during heating and cooling at 1 MHz over a temperature range from 260 K to 300 K.

The interaction energy (energy Keesom) of two oppositely directed dipoles will be determined by the relation:

$$W_1 = \frac{1}{4\pi\varepsilon_o}\frac{2p_1p_2}{r_{12}^3}, \tag{2}$$

While in paraelectric phase, ready dipole moments of $PbTiO_3$ microparticles interact with induced dipole moments in NH_4HSO_4 with energy (Debye energy):

$$W_2 = \frac{\chi}{4\pi^2\varepsilon_o^2}\frac{2p_1^2}{r_{12}^6}, \tag{3}$$

where χ – polarizability. This energy has a lower value and decreases proportionally to the sixth power of the distance. The difference in free energy of expansion when approaching from above and below by the phase transition temperature leads to a jump in energy; therefore, the phase transition changes its order from II to I.

4. Conclusion

Dielectric studies of ferroelectric composite $(NH_4HSO_4)_x/(PbTiO_3)_{1-x}$ have shown that the value of the temperature interval of existence of the ferroelectric phase increases by ~5 degrees and it is independent at the volume fraction of particulate inclusions in composites. Revealed temperature hysteresis of the upper phase transition may indicate a change in the type of phase transition from the second order to the first order one.

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